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Ancient Mercury-Based Plating Methods: Combined Use of Surface Analytical Techniques for the Study of Manufacturing Process and Degradation Phenomena

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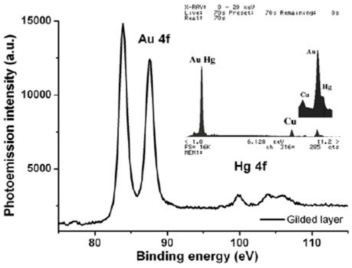
CONSPECTUS

Fire gilding and silvering are age-old mercury-based processes used to coat the surface of less precious substrates with thin layers of gold or silver. In ancient times, these methods were used to produce and decorate different types of artefacts, such as jewels, statues, amulets, and commonly-used objects. Gilders performed these processes not only to decorate objects but also to simulate the appearance of gold or silver, sometimes fraudulently. From a technological point of view, the aim of these workmen over 2000 years ago was to make the precious metal coatings as thin and adherent as possible. This was in order to save expensive metals and to improve the resistance to the wear caused by continued use and circulation.

Without knowledge about the chemical–physical processes, the ancient craftsmen systematically manipulated these metals to create functional and decorative artistic objects. The mercury-based methods were also fraudulently used in ancient times to produce objects such as jewels and coins that looked like they were made of silver or gold but actually had a less precious core. These coins were minted by counterfeiters but also by the official issuing authorities. The latter was probably because of a lack of precious metals, reflecting periods of severe economic conditions.

In this Account, we discuss some representative cases of gold- and silver-coated objects, focusing on unique and valuable Roman and Dark Ages period works of art, such as the St. Ambrogio's altar (825 AD), and commonly used objects. We carried out the investigations using surface analytical methods, such as selected area X-ray photoelectron spectroscopy and scanning electron microscopy combined with energy-dispersive spectroscopy. We used these methods to investigate the surface and subsurface chemical features of these important examples of art and technology, interpreting some aspects of the manufacturing methods and of disclosing degradation agents and mechanisms. These findings may contribute to cultural heritage preservation, thus extending the applicability of the surface analytical techniques.



Introduction

Since the 18th century eminent scientists, such as Berzelius, Faraday, Berthelot, and Röntgen, used analytical methods to identify the chemical composition of ancient coins, glasses, pigments, and ceramics. The pioneering approach has continued through recent centuries, and many material

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scientists have studied works of art or commonly used objects in order to determine their chemical composition, structural features, and degradation products in order to understand how they were manufactured or the origin of the raw materials used.[1,2]

The development of new analytical methodologies, their continuous improvement, and their use in the field of cultural heritage have recently allowed us to obtain a wider range of information concerning the origin and mechanisms of material decay,[1−5] thus opening up innovative tailored approaches for the design and validation of innovative and reliable conservation materials, which ensure a long and stable life for ancient artifacts.

The commonly used techniques for these studies generally probe the bulk chemical and structural characteristics of the objects and overlook surface features, often essential for understanding manufacturing techniques and degradation processes. In this field, investigators have occasionally used surface analytical techniques,[5−7] such as X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and glow discharge optical emission spectrometry (GDOES). They have shown that these techniques complement the more commonly used analytical surface methodologies, such as scanning electron microscopy (SEM) and μ-Raman spectroscopy and are a significant breakthrough in the study of cultural heritage.

Owing to the advantages afforded by the above listed methodologies for extracting detailed chemical and morphological information in a depth range from a few nanometers to submicrometer, and the possibility of identifying the presence and chemical state of essentially the entire Periodic Table, the combined use of XPS and SEM-EDS techniques can disclose the complex micro- and nanochemical surface nature of ancient artifacts; specific questions related to manufacturing techniques and degradation phenomena are therefore answered.

With these aims in mind, the above-mentioned nondestructive and nano- or microdestructive methods have been used for detailed study of thin layers of gold or silver deposited via amalgam techniques by artists and metallurgists from these ancient times. On the basis of their long-term cognitive skills, these latter perceived that the surface of metals could be modified via empirically optimized treatments for both artistic and functional purposes. They created unique and functional features, as well as giving the deliberate impression that the objects were made entirely of gold or silver.[8−10]

The hereafter described results confirm the analytical capabilities of the surface techniques and evidence the high level of competence reached by the artists and craftsmen of these ancient periods who produced objects of an artistic quality that could not be bettered in ancient times and has not yet been reached in modern ones.

Mercury-Based and Other Sophisticated Ancient Coating Techniques

Over 2000 years ago, artists and metallurgists used various methods for applying a metallic layer to an object, from the simple folding of a leaf around the artifact to more multistep and complex processes,[8−18] which were occasionally considered closely guarded secrets.

The following are brief descriptions of the techniques used in ancient times that can be considered the most interesting from a chemical−physical point of view:

- **Depletion Gilding**. According to this subtractive method, a copper-based object can be surface-enriched with a layer of precious metal by means of repeated cycles of thermal treatments and selective removal of copper. Pickling solutions, such as salts and organic compounds, which etched away the oxidized copper leaving a silver or gold spongy crust on the surface were used.[7,11,17] This latter is then burnished, leaving a brilliant and more attractive polished finish.
- **Macro or Inverse Segregation**. This latter phenomenon could occur during the solidification of a copper-based alloy under specific cooling parameters; tin, arsenic, or antimony can be forced to the interdendritic areas and to the surface of the object, thus forming species with a silver-like appearance. An example of artifacts coated by this method are the "Lybian war" coins minted by Carthaginians in North Africa (241−238 BC) during the war between Carthage and the Libyan rebels after the First Punic War.[19] The surface of these coins were As−Sb-enriched by thermally pushing As and Sb contained in the copper core to the external region of the cast blank via inverse macrosegregation, thus creating a silver-like surface. The expertise of Carthaginian metallurgists was based purely on empirical skills, since they were able to observe phenomena and then to replicate them. It is worth noting that this method was also used by Romans to form a reflective and corrosion-resistant δ-$Sn_{31}-Cu_8$ film on bronze mirrors and during the Renaissance in Italy for issuing coins with a surface enriched with a silver−antimony alloy.
- **Mercury Silvering and Gilding**. This low-temperature coating method was developed in China from the 4th to the 3rd century BC, and then it was likely transmitted to the Mediterranean basin via the silk route

in the 1st century BC. It was used as a less expensive alternative method to deposit thinner adherent films of gold or silver on works of art, jewels, decorative items, and forgeries.[8−11,14] The method was used widely and successfully due to its unique decorative effects, the consistent saving of precious metals, and the consequent increase of profit. By the 2nd and 3rd century AD, the use of mercury-based methods was rapidly expanded in Europe. It was the predominant gold coating technique until the invention of electroplating in the mid-19th century when mercury-gilding fell into disuse because it was more expensive, and the threat of mercury toxicity became known. There are two different methods for mercury gilding and silvering.[8−13] The first one is based on the use of mercury as a "glue" to apply a gold leaf by forming an amalgam at the substrate−leaf interface, that is, cold mercury gilding. The second method is a solid-state reaction based on the use of an amalgam of gold or silver and mercury, produced by grinding Au or Ag dust with mercury and gently brushing the amalgam paste on a clean and oxide-free metal substrate to be coated. A thermal treatment was then carried out at about 250−350 °C, below the boiling point of mercury (357 °C); this was done for a few minutes in air in order to volatilize the mercury and leave a gold or silver film with a residual presence of mercury.[8−10] Because of its unevenness and porosity, the final finishing was carried out mechanically by means of a metal, bone, or stone burnisher to gently compress the porous structure in order to create a smooth, shiny surface, similar to that of gold or silver.[11−13]

This Account illustrates the chemical and structural features of a thin metal layer produced by using the mercury-based technique. For this purpose, we have first investigated a gold layer, which was prepared appositely by mercury gilding. The micro- and nanostructure and the chemical composition of a gold amalgam are shown in Figure 1 by SEM images and EDS spectra; they are shown both after a partial evaporation of mercury and after the overall treatment. These latter results reveal that the surface is porous and composed of small round grains whose size ranges from 200 nm to about 1 μm. It is worth noting that the nanoporosity of the gold layer could have a detrimental effect during burial because it could act as nanochannels along which the anions coming from the soil could corrode the less noble substrate.

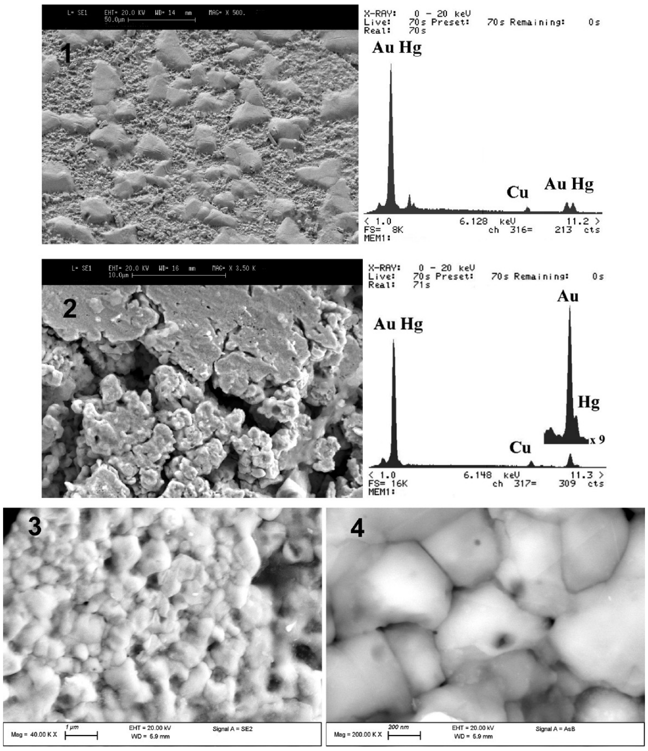

FIGURE 1. The morphology and surface chemical composition of the Au−Hg amalgam after mild thermal treatment carried out at 250 °C for 2 and 15 min (images 1 and 2, respectively). High-resolution SEM images for the gold layer after the overall thermal treatment (images 3 and 4) show that the surface is porous due to Hg evaporation and composed of small round gold grains containing a noticeable amount of Hg (about 12 wt %), whose diameter ranges from 200 nm to 1 μm.

EDS results reveal that the thermal treatment does not remove the mercury entirely; it is retained in the precious metal in noticeable amounts ranging from a few weight percent for gold-coated objects, to about 25−30 wt % for silver-coated ones. The amount of residual mercury depends on the nature of the precious metal, and the adopted technological parameters, such as temperature and duration of heat treatment, as well as on the Ag or Au/Hg ratio in the amalgam. The experimental details depended on the artist's skill, the size of the object, and the desired thickness of the gold or silver layer.

For the above-mentioned reasons, fire gilding is easy to detect because mercury is never removed completely by the heating process, and the Hg residual content can be detected by surface analytical techniques, which allow the identification of the manufacturing method.

Surface Studies of Coated Objects

This Account provides some representative examples of the chemical nature and micro- and nanostructure of thin gold or silver layers produced via the mercury-based coating technique by artists and craftsmen in ancient periods. These techniques manipulated and combined metals to create

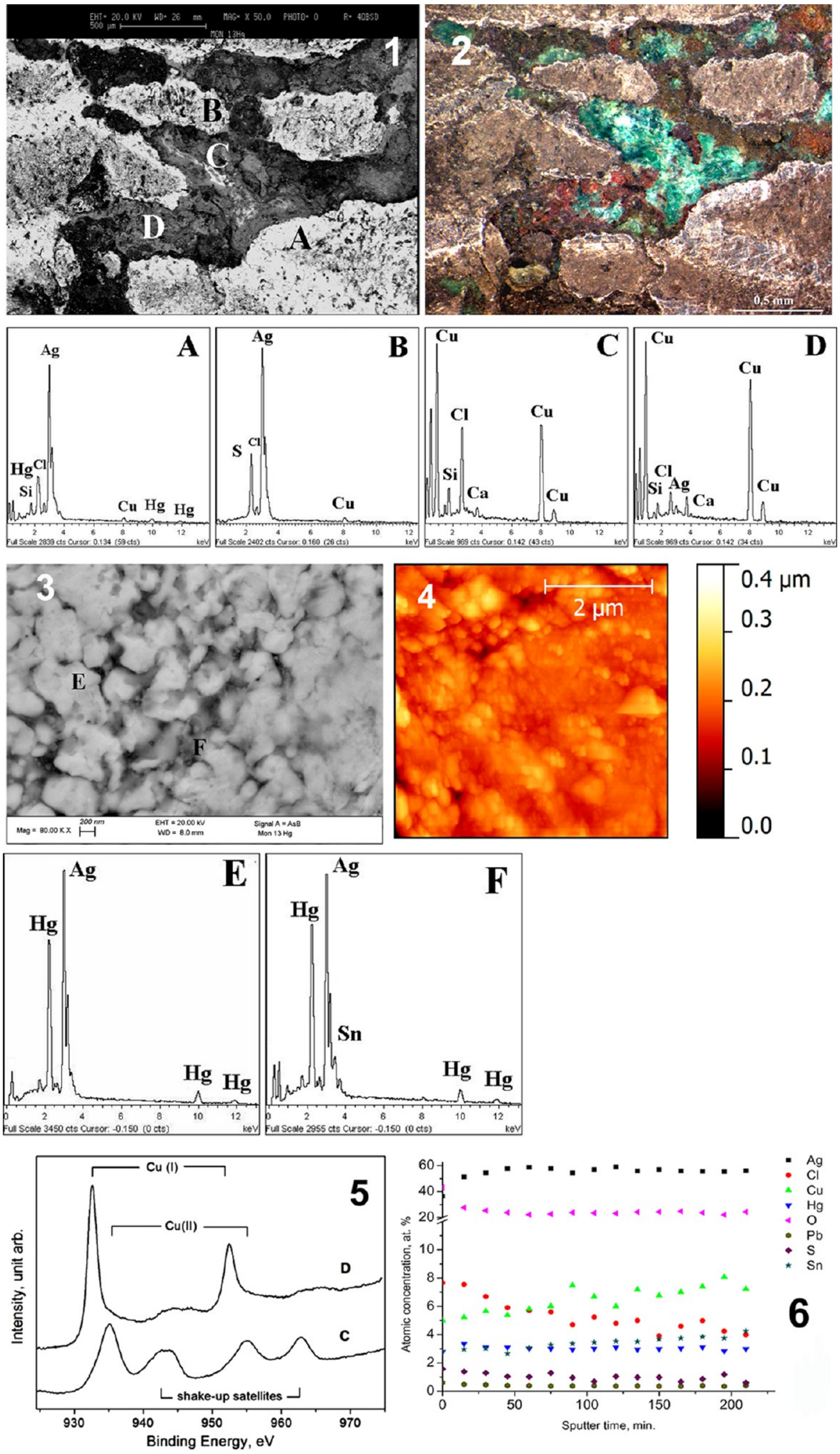

FIGURE 2. The morphology and surface chemical composition of a Republican Roman copper coin coated with a thin silver layer by using a Ag–Hg amalgam. The optical and backscattered electron images (1–3) combined with EDS spectra (A–F) taken on the areas where the precious metals are still present clearly show the presence of mercury in the thin metal layer. SEM and AFM images (3, 4) demonstrate that the surface is composed of small grains and subgrains whose diameters range from 100 nm to 1 μm. The areas where the precious metal is absent are characterized by the presence of different copper corrosion products, including cuprite (Cu_2O) and the dangerous atacamite [$CuCl_2 \cdot 3Cu(OH)_2$]. The XPS spectrum (5) shows the presence of Cu(I) and Cu(II) species, whereas the XPS concentration depth profile (6) reveals the presence of different elements from the soil (Ar^+ etching rate about 0.2 nm/min) on the *patina*.

TABLE 1. Binding Energy (BE) and Modified Auger Parameter (α') of Reference and Investigated Samples

reference materials and analyzed area of the artifact	BE value of Cu $2p_{3/2}$ (eV)	α' (eV)	Cu oxidation state
Cu (99.9%)	933.0	1851.5	0
Cu_2O (cuprite)	932.6	1849.5	+1
CuO (tenorite)	933.8	1851.5	+2
CuCl (nantokite)	933.1	1848.7	+1
$CuCl_2$ (tolbakite)	935.5	1850.9	+2
Republican Roman copper coin, reddish area	932.6	1849.5	+1
Republican Roman copper coin, greenish area	935.2	1851.8	+2

unique functional features on the surface of different metal objects.

Some representative case studies related to gold- and silver-coated artifacts, such as commonly used Roman objects, coins, and works of art including a fragment of a statue and the St. Ambrogio's altar dated to the Dark Ages (825 AD), are discussed herein.

The first case describes the surface micro- and nanochemical and morphological features of a silver-coated Republican Roman copper coin (*denarius*, 1st century BC) that is considered one the most ancient precisely dated artifacts coated via mercury-based method in the Roman world and possibly in Europe.

SEM, atomic force microscopy (AFM), and optical microscopy (OM) images combined with XPS and EDS spectra represented in Figure 2 show the complex morphology and surface chemical composition of this coin and evidence that the corrosion that occurred during long-term burial has greatly affected the integrity of the thin silver layer causing only a small amount of the plating to remain *in situ*. Indeed, copper corrosion products have erupted through the silver layer in several places and have forced the precious thin metal layer outward.[7,20] The backscattered electron images and EDS spectra taken on the areas where the precious metals are still present clearly show the presence of mercury in the thin metal layers, thus demonstrating the use of a Ag–Hg amalgam. The EDS spectra disclose that the amount of Hg is higher with respect to the content usually measured in a gilded object. This is because silver has a high solid solubility for mercury.[21]

In order to gain further insight into the chemical species formed by the degradation phenomena, selected area X-ray photoelectron spectroscopy (SA-XPS) investigations have been performed, cooling the sample with liquid nitrogen to prevent X-ray and ion induced chemical modification.[22] The results are reported in Table 1 and demonstrate that the areas where the precious metal is absent are characterized by the presence of copper corrosion products including cuprite (Cu_2O) and the dangerous atacamite [$CuCl_2 \cdot 3Cu(OH)_2$], that is, the compound produced from the destructive copper cyclic corrosion reaction roughly defined as "bronze disease".[20]

Indeed, the binding energy (BE) value of the Cu $2p_{3/2}$ photoemission signal measured in the reddish areas, whose value is 932.6 eV, is assigned to Cu(I) oxide.[22,23] This result is also supported by the modified Auger parameter, defined as $\alpha' = \mathrm{BE(Cu\ 2p_{3/2}) + KE(Cu\ LMM)}$, whose value is 1849.5 eV. A second contribution at BE of 935.2 eV is assigned to Cu(II) oxides, according to the low intensity shakeup satellites positioned at BE = 944.2 eV. The Cu $2p_{3/2}$ signal measured in the greenish areas peaked at 935.2 eV, and it is characterized by intense shakeup satellites, typical for the Cu^{2+} oxidation state.[22,23] This information, combined with the value of the α' Auger parameter (1851.8 eV) and the line shape of the photoemission peak, allow atacamite [$CuCl_2 \cdot 3Cu(OH)_2$][24] to be assigned to the Cu(II) species and the identification of chloride ions as main degradation agents.

Concerning tin, whose presence is also revealed by EDS spectra, located between the silver–mercury grains, the BE of the main peak Sn $3d_{5/2}$ is positioned at 486.7 eV, which corresponds to a Sn(IV) oxidation state.[25–27] The observed surface tin enrichment on the *patina* could likely be related to the selective dissolution of copper or to the oxidation of tin from the substrate that travels along the nanoporosity of the silver–mercury layer and precipitates as tin oxide on the external surface of the coin. This hypothesis is also supported by the absence of tin in the inner region of the thin mercury–silver layer, excluding the presence of tin in the silver–mercury amalgam.

The use of the mercury silvering technique is confirmed by the photoemission signal of Hg 4f that reveals the presence of two different components at BE of 100.4 and 101.9 eV, which are assigned to Hg^0 and Hg^{2+} (as Hg–Cl), respectively.[28] Regarding the silver XPS signal, the Ag $3d_{5/2}$ peak at BE = 368.6 eV and the modified Auger parameter, $\alpha' = 725.6$ eV, suggest that silver is mainly in the metallic state with a low amount of chloroargyrite (AgCl) and silver sulfide (AgS) in the outermost layers. This assignment is confirmed by the BE values of S 2p and Cl 2p at BE = 161.7 eV and BE = 199.0, respectively, typical of sulfide and chloride chemical bonding.

Chloroargyrite is commonly observed on archeological silver objects, and the copper chlorides and oxi-chlorides are typical components of bronze *patinas*, whereas sulfides of silver or copper have rarely been observed as corrosion products on silver or bronze archeological artifacts and have been detected mainly on objects found in seawater or lake sediments.[27] Indeed, the ubiquitous and nearly constant presence of chloride ions is always observed in the *patina* of Ag-based and Cu-based artifacts found in different contexts of the Mediterranean basin, indicating that the main degradation agent is chlorine.[7,20,27] Finally, XPS has revealed a low content of Pb as lead chloride (BE = 139.6 eV) on the outermost layers. The elemental XPS concentration depth profiles of the silver-coated Roman coins are shown in Figure 2. In this graph, the adventitious carbon contamination has not been clearly reported. Indeed, the carbon content quickly dropped from about 25 atom % to lower values (15−10 atom %) after a few minutes of Ar^+ etching and disappeared after about 150 min.

XPS elemental depth profiles combined with EDS spectra reveal the presence of different copper compounds, such as oxychloride and oxide species, and other elements, such as Cl, S, Si, Al, and Ca, in the external areas of the *patina*. The latter usually derive from the soil, revealing the strong interaction with the elements constituting the coin. This interaction gives rise to the formation of different corrosion products during the burial, the character of which is remarkably affected by the nature of the soil and of the artifact. Furthermore, we must consider the peculiar corrosion behavior of coated artifacts, which contain metals with different electrochemical potential. The presence of soil components and water is responsible for an electrical connection between the metals, acting as an electrolyte. This contact induces the oxidation of the less noble metal, which become anodic and promotes the degradation of the object. The amount of current that flows and, therefore, the extent of corrosion depend on many variables, among which are the chemical−physical parameters of the burial context, the difference in electrochemical potential of the two metals, the presence and nature of the electrolyte, and the microchemical structure and metallurgical features of the alloy. These factors can induce dramatic selective corrosion phenomena in copper, transforming the substrate into cuprite (Cu_2O) and other copper−chlorine degradation products.

The second case illustrates the surface micro- and nanochemical and morphological features of a silver-coated Roman statue. Unfortunately, archeologists have found only a part of this object, which was a Roman lion statue dating back to the 2nd century AD. The statue fragment represents the right hind leg of an advancing lion and consists of an internal ceramic core with a 300 μm thick foil of copper coated with a thin film of silver wrapped around it. Its general appearance demonstrates that the ancient craftsmen were able to produce an artifact with a complex shape that was uniformly coated, thus obtaining the aspect of a solid silver object, as well as saving a relevant amount of silver.

This work of art was selected in order to show the minimum thickness of a silver layer achievable by the Romans. The back scattered electron SEM image and EDS spectra of the metallographic cross-section in Figure 3 reveal that the coating was deposited by using a silver−mercury amalgam, as demonstrated by the presence of mercury in the silver layer (Figure 3). The thickness of the Ag−Hg film is about 1 μm and corresponds to the surface white layer in the back scattered electron image. These findings demonstrate that the layer is still present on a large part of the artifact, even though cuprite crystals (Cu_2O) have grown at the interface between the silver layer and the partially corroded copper substrate. Furthermore, the optical image shows that cuprite (Cu_2O) has erupted through the gilding only in several places and has forced the gilding outward, thus corrugating the thin silver film.

Another valuable artifact that we have investigated is a gilded Medieval copper decorative object. Some selected SEM-EDS, AFM, OM, and XPS results are shown in Figure 4. The OM images provide evidence that a large part of the plating remains *in situ,* and the thin layer of gold is still present and visible in large areas of the artifacts, even though in some regions it has been removed by the eruption of reddish-brown cuprite (Cu_2O) through the gilded layer. The AFM in image 3 reveals that the surface is composed of small round grains and subgrains whose diameters range from 40 nm to approximately 200 nm.

Investigations, SA-XPS, were performed in order to quantify the amount of Hg contained in the outermost layer of the gold-coated objects. Figure 4 shows the comparison between the photoemission Au 4f and Hg 4f signals for the artifact, with a Au−Hg amalgam and pure gold as reference. Moreover, the elemental depth profile of the gold layer is shown in Figure 4 as a function of Ar^+ sputtering time, starting from the surface in as-received state and using an etching rate of about 0.2 nm/min.

The line shape analysis of the Au $4f_{7/2}$−Au $4f_{5/2}$ photoemission signals reveals a broadening of the 4f peaks for the gilded and amalgam layers compared with those of the Au

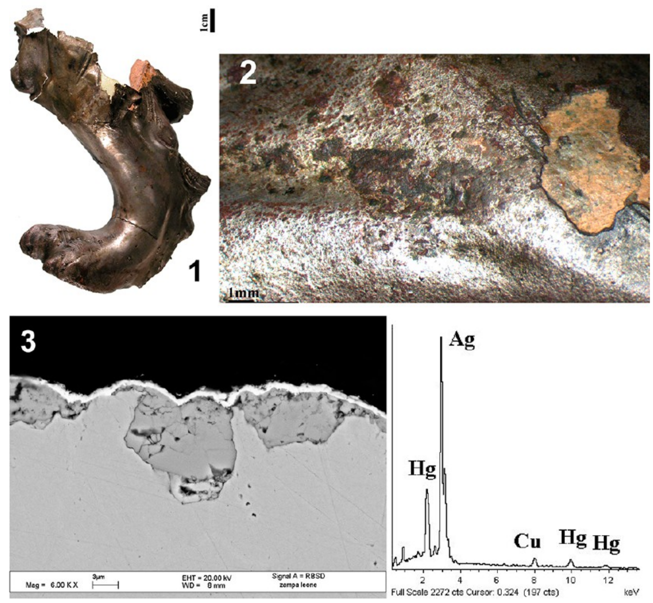

FIGURE 3. Part of a Roman lion statue dating back to the 2nd century AD and found close to Rome. The statue represents the right hind leg of an advancing lion (1) and the OM image (2) shows that it consists of an internal ceramic core with a wrapped foil of copper coated with a thin silver film. The backscattered SEM image (3) and the EDS spectrum for metallographic cross-section reveal that the thickness of silver film is about 1 μm and is composed of a Hg–Ag amalgam.

reference material. Even if all samples are characterized by a single Au $4f_{7/2}$ peak at the same BE, which is 84.0 eV, the increase of the full width at half-maximum of the Au 4f peaks is related to the disorder in the lattice caused by the presence of mercury.

In contrast, the peak-fitting of the Hg $4f_{7/2}$ signal of the gilded object is characterized by the presence of two components assigned to Hg^0 (BE = 99.8 eV) and to Hg^{2+} (BE = 103.0 eV). This result demonstrates that the mercury is subjected to chemical modification induced by the burial context. This could be related to the presence of chlorides (BE = 199.8 eV) and sulfides (BE = 168.6 eV) revealed by the XPS analysis, whose amount is less than 2–3%. These are aggressive agents that derive from the soil and react with mercury, inducing the chemical modification of the amalgam layer and forming chlorides and sulfides. Moreover, the XPS depth profile shows a decrease of the Hg/Au ratio from the surface to the inner region; this means that the microchemical structure changes through the gilded layer, demonstrating that the surface mercury enrichment is probably due to selective reactions that occurred during the long-term burial.

The SEM image for the cross-sectioned artifact clearly shows the thin and yet adherent mercury-enriched gold layer placed on the partially corroded copper substrate and that the corrosion phenomenon has proceeded along the nanoporosity of the layer, acting as channels along which the anions coming from the soil corrode the less noble copper substrate.

Concerning the chemical nature of the substrates, our investigations have shown that the craftsmen of the classical age often used nearly pure copper substrates; this was due to the difficulties encountered in mercury gilding artifacts that consisted of tin–copper alloys. When these alloys were used, a brittle tin–mercury amalgam and tin oxides could be formed at the interface between gold and substrate during the final heating stage of the fire-gilding process.

This process was carried out to evaporate as much mercury as possible; this is so that the gold layer is not firmly adherent and can be easily removed.

Mercury was also used by barbarians such as the Goths, Longobards, and Vandals for coating luxury objects, for example, buckles and brooches. It was also used by goldsmiths of the so-called Dark Ages, following the collapse of the Western Roman Empire, for obtaining a decorative effect. This was achieved by combining noble and less-precious metals with enamel, thus producing unique and fascinating jewels and works of arts, such as the following described case study: the golden altar of the Holy Ambrogio in Milan (Italy).

The altar is considered to be one of the most important works of art produced by a goldsmith and is composed of a rectangular wooden case (250 cm ×120 cm × 130 cm), on the walls of which are large panels of gold, silver, and gold-plated silver decorated with precious enamels, filigrees, and many different gems, such as emerald, topaz, amethyst, agate, and carnelian.

The altar was given to the Holy Ambrogio basilica by Angilbertus II, who was Archbishop of Milan from 829 to 859 AD. It was manufactured by a goldsmith named Volvinius who used his great experience to utilize the color contrast of gold and silver. His technique involved painting the silver panels with gold in order to produce fascinating decorative effects.

The aim of our study was to gain further insights into the nature of the gold layer applied onto the silver panels and on the coating technique. A further objective was to determine the state of preservation of the altar.

SEM and EDS results for the cross-section of the silver-gilded panel shown in Figure 5 and Table 2 allow us to identify the coating technique that was based on the local use of mercury–gold amalgam. A description of the microchemical structure of the gold layer and the complex

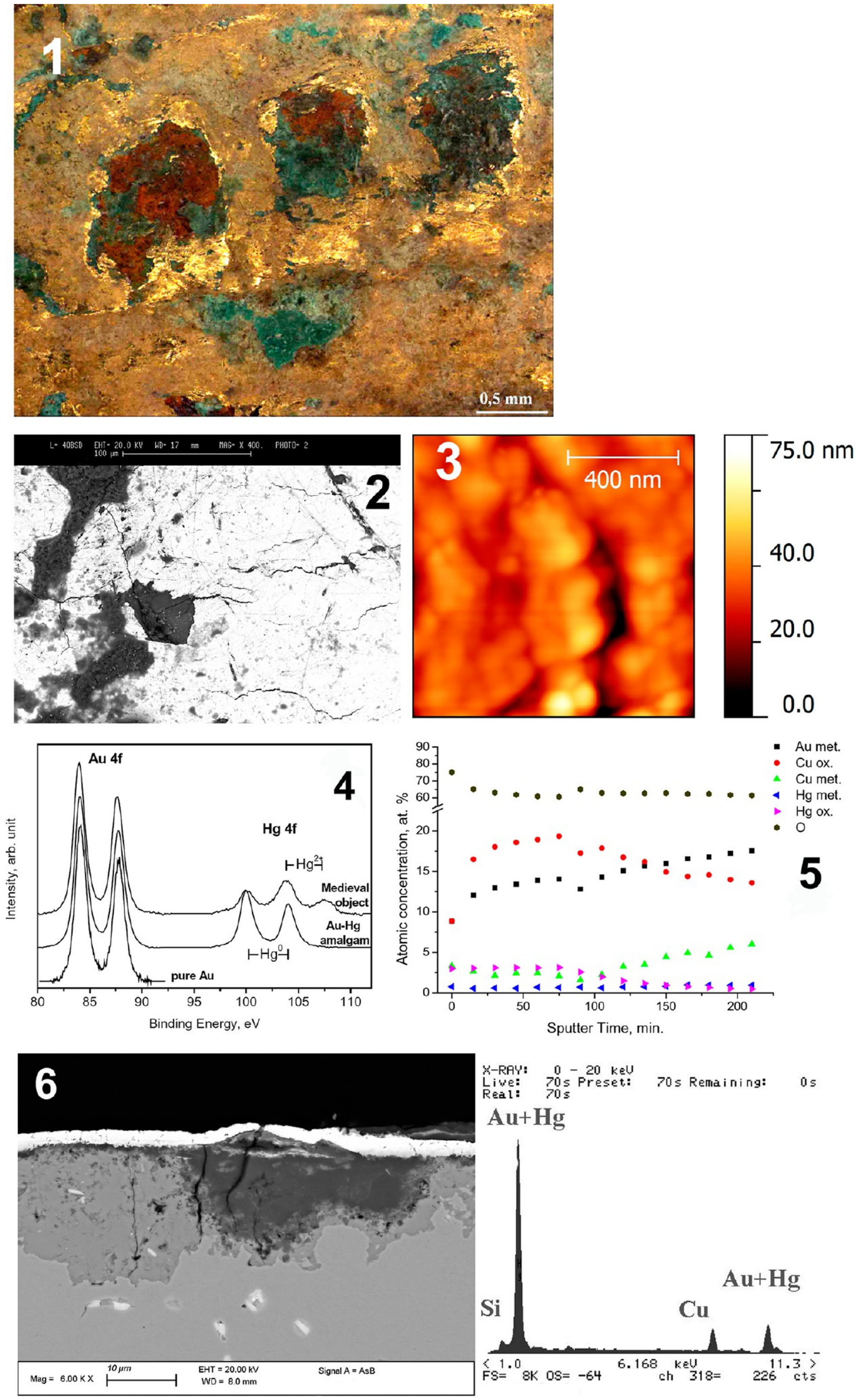

FIGURE 4. Details of a Medieval gilded copper decorative object. The OM and SEM images (1, 2) show that the gold plating is still well adhered in large areas of the artifact and was only partly removed by the eruption of reddish-brown cuprite. The AFM image (3) reveals that the surface is composed of small round grains and subgrains whose diameters range from 40 nm to about 200 nm. XPS spectra and elemental concentration depth profiles (4, 5), combined with SEM-EDS results of the cross-section (6), disclose the chemical nature and the thickness of the thin Hg-enriched gold layer. The depth profiles of Cl and S have not been shown, their concentrations being lower than 2–3 atom % and decreasing in the inner layer.

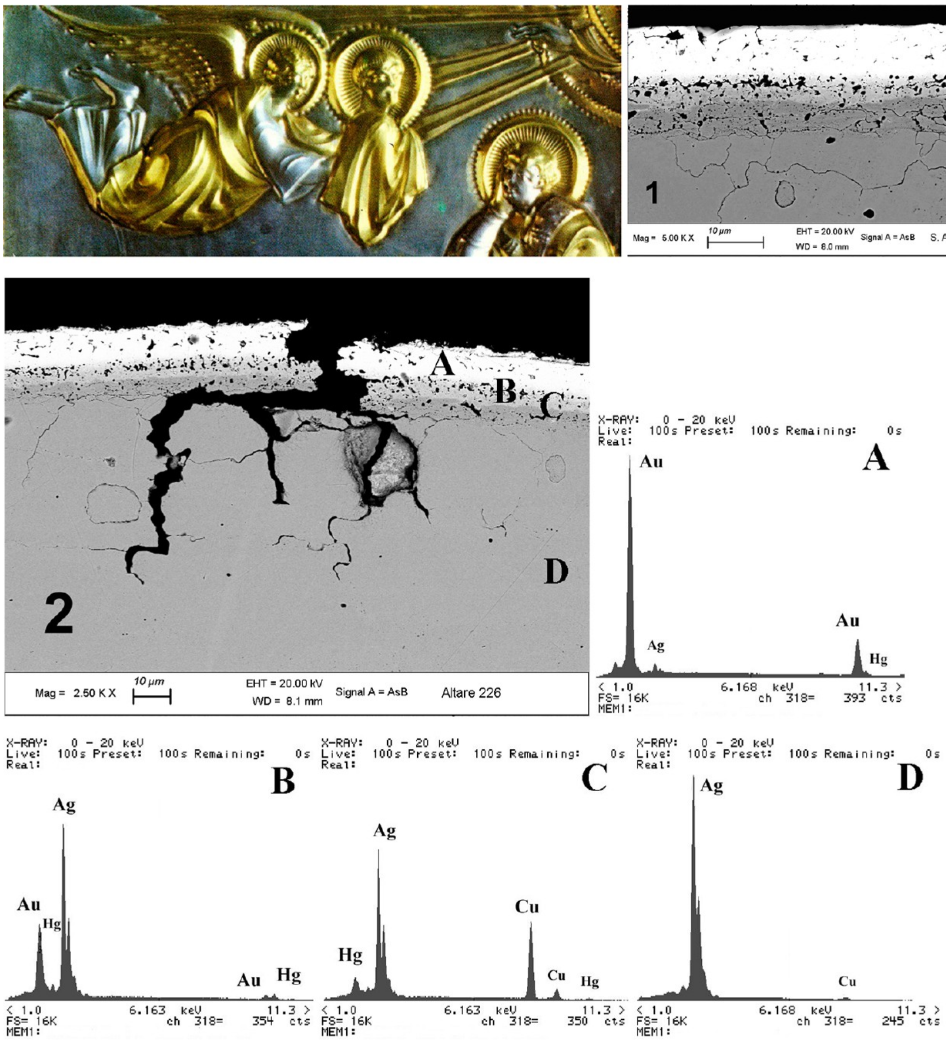

FIGURE 5. A detail of a gilded panel of the Holy Ambrogio golden altar. The figures in relief from the silver substrate have been "painted" with a thin layer of gold via mercury gilding to achieve a lustrous effect; this is due to the combination of silver and gold. Backscattered SEM images (1, 2) and EDS spectra for the cross-sectioned silver-gilded panel are shown to disclose the microchemical structure of the external Hg-enriched gold layer, its interface with silver substrate and the region damaged by the presence of cracks.

interface between this latter and the silver substrate was also possible with these results.

In this region, SEM-EDS results reveal the presence of layers with different contents of Hg, Au, and Ag. In particular, the diffusion of mercury into the silver substrate was observed. This probably occurred during the thermal treatment at 250−350 °C, the typical temperature used in the mercury-based gilding process. These findings confirm the high solid solubility of mercury in silver with respect to gold and indicate that in this case the gilding process is a diffusion bonding process in which the role of mercury is also to ensure a close contact between substrate and plating,[8−10] thus promoting a good adhesion. Furthermore, the results show the presence of microcracks and a dense population of cuprite (Cu_2O) microglobules that formed during the manufacturing of the panel. This is probably due to the repeated mechanical cycles for flattening silver and the thermal treatments for annealing it.

In some areas of the panel, the presence of intergranular cracks is clearly evident. These latter were not caused by corrosion but by an aging phenomenon inducing brittleness. This is because silver must have been quite ductile when the panels were manufactured and decorated. The brittleness of ancient silver objects has often been observed in the coins of ancient Greece, Saxon, and England and the Late medieval coins of India, as well as in Roman and Egyptian silver artifacts.[6,29,30] This type of brittleness therefore has a wide geographical and historical distribution and cannot result from corrosion due to the absence of corrosion products. It could be related to aging phenomena that induce the

TABLE 2. EDS Chemical Analysis of the Different Regions of the Cross-Sectioned Silver-Gilded Panel[a]

analyzed area, spectrum	Au (wt %)	Hg (wt %)	Ag (wt %)	Cu (wt %)
gold external layer, spectrum A	88.9	5.9	5.2	
gray layer under the gold layer, spectrum B	9.6	23.4	64.7	2.3
gray layer under the gold layer[b]	10.5	21.5	62.3	5.7
black phases at the interface gold–silver, spectrum C	3.5	12.5	39.4	44.6
black phases at the interface gold–silver[b]		7.4	59.5	33.1
nanophases at the interface gold–silver[b]		7.6	64.1	28.3
silver substrate, spectrum D	0.5		94.6	4.9
silver substrate[b]	0.7		95.1	4.2

[a] See Figure 5. [b] Spectrum not shown in Figure 5.

segregation of impurities along grain boundaries, modify the metallurgical features and reduce the cohesive strength.[6,29,30] The occurrence of these latter detrimental phenomena, combined with repeated cycles of mechanical expansion and contraction of the wooden case induced by repeated changes of environmental conditions, are probably responsible for the formation of microcracks.

Conclusions

This Account highlights the relevance of surface analytical techniques for the investigation of ancient coated artifacts in order to decipher the deposition technologies and to identify the degradation agents and mechanisms to contribute to their preservation, valorization, and fruition.

The reported results indicate that over 2000 ago important advances in the technology of thin film deposition on metal substrates were attained using mercury-based plating methods. This allowed the production of adherent precious metal layers with a uniform thickness ranging from one to a few micrometers on commonly used objects and works of art with complex shapes, as well as on forgeries resistant to the wear of use and circulation.

Surface analytical methods have demonstrated the high level of competence of the Roman and Dark Ages goldsmiths and well document the improvements in the thin film coating technology achieved by mercury-based methods.

Moreover, the combined use of surface analytical techniques has allowed a significant breakthrough in the identification of degradation agents and processes, which are usually related to the composition of coated artifacts and the burial context, as well as disclosed peculiar chemical and nano- or micromorphological features useful to verify the authenticity of cultural heritage objects. The investigation of the surface layers in a depth range from a few nanometers to submicrometer also revealed the complex micro- and nanochemical nature of corrosion products, answering specific questions related to the peculiar degradation mechanisms and segregation phenomena thus extending the impact of the surface analytical techniques.

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FOOTNOTES

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REFERENCES

1 Brunetti, B. G.; Sgamellotti, A.; Clark, A. J. Advanced Techniques in Art Conservation. *Acc. Chem. Res.* **2010**, *43*, 693–694.

2 Romani, A.; Clementi, C.; Miliani, C.; Favaro, G. Fluorescence Spectroscopy: A Powerful Technique for the Noninvasive Characterization of Artwork. *Acc. Chem. Res.* **2010**, *43*, 837–846.

3 Melcher, M.; Wiesinger, R.; Schreiner, M. Degradation of Glass Artifacts: Application of Modern Surface Analytical Techniques. *Acc. Chem. Res.* **2010**, *43*, 916–926.

4 Adriaens, A.; Dowsett, M. The Coordinated Use of Synchrotron Spectroelectrochemistry for Corrosion Studies on Heritage Metals. *Acc. Chem. Res.* **2010**, *43*, 927–935.

5 Spoto, G.; Torrisi, A.; Contino, A. Probing Archaeological and Artistic Solid Materials by Spatially Resolved Analytical Techniques. *Chem. Soc. Rev.* **2000**, *29*, 429–439.

6 Ingo, G. M.; Angelini, E.; Bultrini, G.; De Caro, T.; Pandolfi, L.; Mezzi, A. Contribution of Surface Analytical Techniques for the Microchemical Study of Archaeological Artefacts. *Surf. Interface Anal.* **2002**, *34*, 328–336.

7 Ingo, G. M.; Angelini, E.; de Caro, T.; Bultrini, G. Combined Use of Surface and Micro-Analytical Techniques for the Study of Ancient Coins. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *79*, 171–79.

8 Anheuser, K. The Practice and Chracaterization of Historic Fire Gilding Techniques. *JOM* **1997**, *49*, 58–62.

9 Anheuser, K. Cold and Hot Mercury Gilding of Metalwork in Antiquity. *Bull. Met. Mus.* **1996**, *26*, 48–52.

10 Anheuser, K. Amalgam Tinning of Chinese Bronze Antiquities. *Archaeometry* **2000**, *42*, 189–200.

11 Oddy, W. A. Gilding: An Outline of the Technological History of the Plating of Gold on to Silver or Copper in the Old World. *Endeavour* **1990**, *15*, 29–33.

12 Lins, P. A.; Oddy, W. A. The Origins of Mercury Gilding. *J. Archaeol. Sci.* **1975**, *2*, 365–373.

13 Oddy, A. Gilding through the Ages. *Gold Bull.* **1981**, *14*, 75–79.

14 Reiff, F.; Bartels, M.; Gastel, M.; Ortner, H. M. Investigation of Contemporary Gilded Forgeries of Ancient Coins. *Fresenius' J. Anal. Chem.* **2001**, *371*, 1146–1153.

15 Zwicker, U.; Oddy, A.; La Niece, S. Roman techniques of manufacturing silver-plated coins. In *Metal Plating and Patination*; Craddock, P.T., La Niece, S., Eds.; Butterworth: Oxford, U. K., 1993; paper no. 20, pp 223−246.

16 Bunker, E. C.; Chase, T.; Northover, P.; Salter, C. Some early Chinese examples of mercury gilding and silvering. In *Outils et ateliers d'orfèvres des temps anciens*; Eluère, C., Ed.; Société des amis du Musée des antiquités nationales et du château de Saint-Germain-en-Laye: Saint-Germain-en-Laye, France, 1993; pp 55−66.

17 Raub, C. J. The Development of Gilding from Antiquity to the Middle Ages. *Mater. Australasia* **1986** (November/December), 7–11.

18 Raub, C. J. How to coat objects with gold-Pliny, Leyden papyrus X, mappae Clavicula and Theophilus seen with a modern chemist's eyes. In *Outils et ateliers d'orfèvres des temps anciens*; Eluère, C., Ed.; Société des amis du Musée des antiquités nationales et du château de Saint-Germain-en-Laye: Saint-Germain-en-Laye, France, 1993; pp 101−110.

19 Carradice, L. A.; La Niece, S. The Lybian War and Coinage: A New Hoard and the Evidence of Metal Analysis. *Numismatic Chronicle* **1988**, *148*, 33–52plates 7−12.

20 Ingo, G. M.; Angelini, E.; Caro, De; Bultrini, G.; Calliari, I. Combined use of GDOES, SEM+EDS, XRD and OM for the Microchemical Study of the Corrosion Products on Archaeological Bronzes. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *79*, 199–203.

21 Rolfe, C.; Hume-Rothery, W. The Constitution of Alloys of Gold and Mercury. *J. Less Common Met.* **1967**, *13*, 1–10.

22 Hayez, V.; Franquet, A.; Hubin, A.; Terryn, H. XPS Study of the Atmospheric Corrosion of Copper Alloys of Archaeological Interest. *Surf. Interface Anal.* **2004**, *36*, 876–879.

23 Schlesinger, R.; Klewe-Nebenius, H.; Bruns, M. Characterisation of Artificially Produced Copper and Bronze Patina by XPS. *Surf. Interface Anal.* **2000**, *30*, 135–139.

24 Mezzi, A.; De Caro, T.; Riccucci, C.; Parisi, E. I.; Faraldi, F.; Vassiliou, P.; Grassini, S. Analytical Methodologies for the Investigation of Soil-Induced Degradation of Cu-Based Archaeological Artefacts. *Surf. Interface Anal.* **2012**, *44*, 953–957.

25 Paparazzo, E.; Fierro, G.; Ingo, G. M.; Zacchetti, N. XPS Studies on the Surface Thermal Modifications of Tin Oxides. *Surf. Interface Anal.* **1988**, *12*, 438–439.

26 Ingo, G. M.; Giorgi, L.; Zacchetti, N.; Azzerri, A. Electrochemical and XPS Studies on Lacquer-Low Tinplated Steel Adhesion. *Corros. Sci.* **1992**, *33*, 361–e77.

27 Ingo, G. M.; De Caro, T.; Riccucci, C.; Khosroff, S. Uncommon Corrosion Phenomena of Archaeological Bronze Alloys. *Appl. Phys. A: Mater. Sci. Process.* **2006**, *83*, 581–588.

28 Briggs, D.; Seah, M. P. *Pratical Surface Analysis*, 2nd ed.; Wiley and Sons Inc.: New York, 1990; p 622.

29 Wanhill, R. J. H.; Steijaart, J. P. H. M.; Leenheer, P.; Koens, J. F. W. Damage Assessment and Preservation of an Egyptian Silver Vase (300−200 BC). *Archaeometry* **1998**, *40*, 123–137.

30 Wanhill, R. J. H. Brittle Archaeological Silver: A Fracture Mechanism and Mechanics Assessment. *Archaeometry* **2003**, *45*, 625–636.